COATINGS

SYNTHESIS OF GLASSES IN THE SYSTEM Na$_2$O – B$_2$O$_3$ – SiO$_2$ FOR COATINGS PROTECTING BRONZE DURING SMELTING

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A system of requirements for unfired process glass coatings for protecting bronze during smelting is formulated and the properties of the coatings are determined. DTA analysis shows the most critical service temperature interval for the new coatings. The initial system Na$_2$ – B$_2$O$_3$ – SiO$_2$ and the initial materials for synthesizing glass coatings on it are chosen. The method of mathematical planning of experiments is used to optimize the composition of the glass flux in the pseudoternary system silicate-block – cullet – borax.

Key words: protective-process glass coatings, composition, smelting of bronze.

Bronze alloys are widely used construction materials. Their main advantages are that they have a high corrosion resistance, heat and electrical conductivity, adequate durability, and low coefficient of friction, and they work at low temperatures (down to – 250°C) and high pressure [1].

The fraction of the bronze which is obtained from secondary initial materials — scrap, production wastes, and secondary alloys — has increased in recent years. Their content in the charge for preparing castings reaches 100% [2]. The use of scrap and nonferrous metal wastes and alloys in casting and blank production is important for addressing diverse problems of shortages of alloy components, ecology, and resource conservation.

Most copper and copper alloy wastes are reprocessed by the group of companies "Vtortsvetmet." Under present-day conditions the wastes formed during metal casting and cast and ingot processing are used directly in production.

When bronze alloys from secondary materials are smelted large losses of these alloys to waste and with slags are observed, reaching in some cases 7 – 10% depending on the smelting method used. In addition, hydrogenation of the melt occurring when the process is conducted in fuel-burning reflective and arc furnaces decreases the quality of the casts. To a lesser extent, these drawbacks are also observed during induction smelting of metal [3].

One of the main ways to eliminate these drawbacks is to use fluxes based on borax, soda, cryolite, fluorspar, low-melting glass, chlorides, and so on [4, 5]. However, existing fluxes do not completely meet industrial requirements for the degree of protection of bronze from oxidation or for surface quality of the alloys; nor do they resolve the problems of supply shortages, ecological safety, and raw-materials costs.

In this connection we are conducting investigations to develop protective-process glass coatings — glass fluxes, which are distinguished by effective protective action during smelting of tin bronze from secondary material and which will not be obtained from ecologically harmful materials (fluorides, chlorides, and others) as well as materials which have a corrosive effect on the furnace lining and are in short supply.

The composition and structure of an unfired protective-process glass coating formed directly during the smelting of bronze must provide adequate gas impermeability and the appropriate degree of coating continuity under conditions where the thermophysical characteristics (heat capacity and thermal conductivity), on which the maintenance of a constant temperature regime depends, are low and at the same time heat losses from the surface of the melt into the surrounding medium decrease.

We have investigated the choice of the initial glass-forming system and the raw materials used to obtain the coatings of the type indicated.

Differential thermal analysis of the behavior of BrO5Ts5S5 tin bronze on heating from 20 to 1000°C (Fig. 1) established that practically no mass changes of the samples of this bronze are observed in the temperature range

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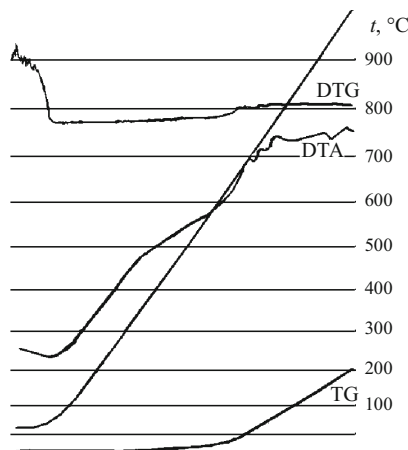[1] National Technical University "Kharkov Polytechnical Institute," Kharkov, Ukraine.

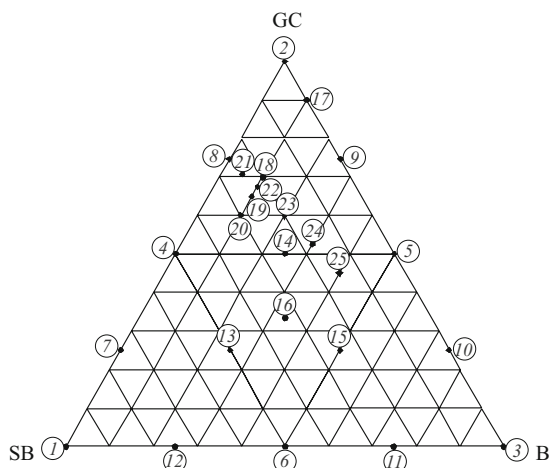**Fig. 1.** Thermogram of BrO5Ts5S5 tin bronze.

Fig. 2. Pseudoternary diagram GC – SB – B.

20 – 600°C, while a linear increase of this parameter is observed in the range 600 – 1000°C. According to the phase diagram of the system Cu – O [6], this is due to intense oxidation of bronze. The rate of this process remains constant even at higher temperatures. As temperature increases from 600 to 1000°C, the weight increase of the bronze changes from 0.1 to 4.5%.

The data obtained made it possible to determine the most critical operating interval for the new coatings (600 – 1000°C) as well as the onset temperature for the formation of a continuous gas-impermeable glass layer (700 – 750°C).

Such indicators of the protective coatings can be attained for certain combinations of the viscosity, density, surface tension, and flowability of the glass melt. These parameters have a considerable effect on the rate at which the liquid flux that is formed spreads over the surface of the metal, the uniformity of the cover thickness, the intensity of the adsorption and dissolution of nonmetallic inclusions in the melt, which float to the surface, as well as the heat transfer between the metal and the surrounding medium.

On this basis and taking account of the requirements for them [7, 8] the fluxes must be characterized by the following system of properties:

minimum gas permeability, so as to avoid oxidation and saturation of the metal with hydrogen under conditions of smelting and contact with the charge, which is directly fed to the surface of the metal melt;

dynamic viscosity in the range $10^3 – 10^4$ Pa · sec, which must be maintained practically constant in the smelting temperature range; any change in the viscosity should not exceed 0.05 Pa · sec [7];

flowability in the interval 30 – 35 mm;

density much lower than that of tin bronze — 8700 – 8800 kg/m^3;

wetting angle no greater than 20° at 1000°C;

surface tension in the range 260 – 290 mN/m;

CLTE of the coating in the solid state less than CLTE of bronze (CLTE for bronze ranges from 166×10^{-7} to 183×10^{-7} K^{-1});

inertness to casting materials and absence of active interaction with the poured metal;

low heat capacity and thermal conductivity;

obtainable from inexpensive raw materials; and,

ecological safety during use [3].

Taking account of these requirements, compositions close to the low-melting eutectic and other invariant points in the system $Na_2O – B_2O_3 – SiO_2$ were chosen as the initial compositions [9] (see Table 1).

The following materials were investigated for synthesis of glass compositions: glass container scrap (GC), ready soluble sodium-silicate glass with modulus 2.73 (silicate block — SB), and borax decahydrate (B). Twenty five compositions differing by the ratio of these materials were investigated in the pseudoternary diagram GC – SB – B (Fig. 2).

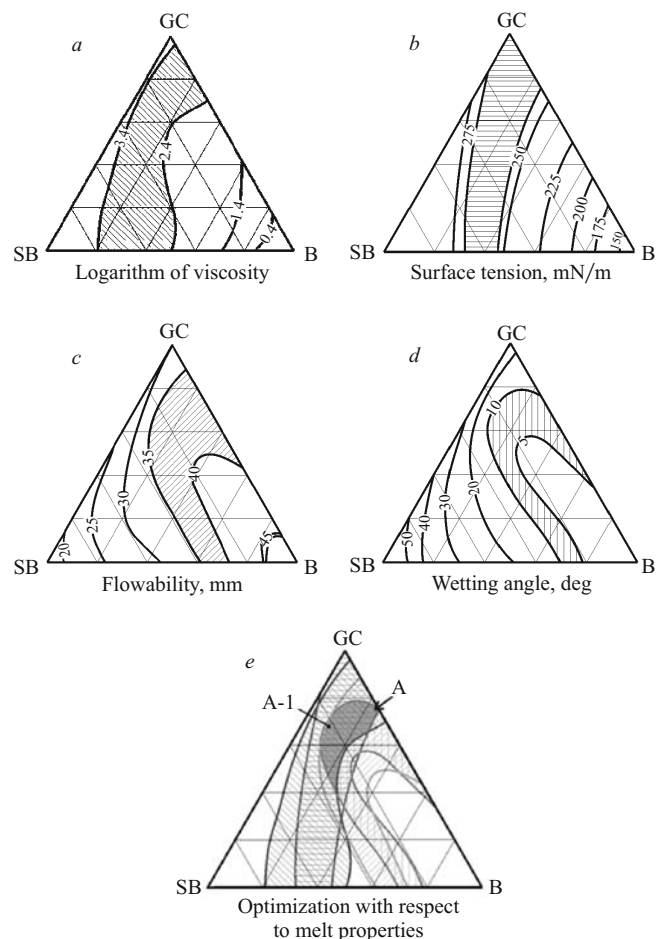These compositions are characterized by the fact that they do not require presintering or smelting; they are used

TABLE 1.

Phase	Content, wt.%			Tempera-ture, °C
	Na$_2$O	B$_2$O$_3$	SiO$_2$	
Na$_2$O · B$_2$O$_3$ + Na$_2$O · 2SiO$_2$ + SiO$_2$ + liquid	27.0	25.0	48.0	520
Na$_2$O · B$_2$O$_3$ + Na$_2$O · 2B$_2$O$_3$ + SiO$_2$ + liquid	27.0	33.0	40.0	520
Na$_2$O · 3B$_2$O$_3$ + SiO$_2$ + Na$_2$O · 4B$_2$O$_3$ + liquid	21.0	45.0	34.0	600
Na$_2$O · B$_2$O$_3$ + Na$_2$O · 2SiO$_2$ + Na$_2$O · SiO$_2$ + liquid	33.0	18.0	49.0	640
Na$_2$O · 4SiO$_2$ + SiO$_2$ + liquid	12.2	55.3	32.5	675
Na$_2$O · 2B$_2$O$_3$ + Na$_2$O · 4B$_2$O$_3$ + liquid	27.7	72.3	–	722
Na$_2$O · B$_2$O$_3$ + SiO$_2$ + liquid	26.9	31.1	42.0	530

Fig. 3. Isolines of the melt properties versus the composition of the glass coating (*a – d*) and the optimal region A with chosen properties A-1 (*e*).

directly in the form of careful prepared mixtures of the initial materials.

The melt properties of the compositions (viscosity, surface tension, flowability, wetting angle) were determined —

the pseudoternary composition – property diagrams were constructed (Fig. 3), and Scheffe's simplex-lattice method of planning experiments was used to optimize the composition ranges corresponding to the complex of requirements which their properties must meet.

TURBO Pascal was used to analyze the experimental data, calculate the coefficients in the polynomial model, check the adequacy of the model, and construct the isolines on the simplex. The composition A-1 obtained in the region A was chosen; this composition is characterized by viscosity $10^{2.7}$ Pa · sec, surface tension 260 mN/m, flowability 35 mm, and wetting angle 10°, which best satisfy the requirements stated for glass fluxes that are suitable for use as unfired protective-process coatings in smelting tin bronze.

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